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**AIR FORCE DEFENSE RESEARCH SCIENCES PROGRAM**

**Kirk Schanze  
UNIVERSITY OF FLORIDA GAINESVILLE**

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## Summary of Accomplishments

*Grant : “Chromophores and Materials for Temporal and Frequency Agile Non-Linear Absorption” Funding Period : Mar. 1, 2009 – Feb. 28, 2014*

This research program focused on development of organometallic chromophore systems for application in temporal and frequency agile non-linear absorption materials. The chromophores that were investigated combine polarizable  $\pi$ -conjugated organic moieties linked to a heavy metal center such as Pt(II) or Ir(III). The  $\pi$ -conjugated organic chromophores are specifically designed so that they exhibit high 2PA absorption cross section ( $\sigma_2$ ), and the heavy metal centers promote singlet  $\rightarrow$  triplet intersystem crossing (ISC) to produce long lived triplet excited states. We and others have shown that these organometallic chromophores exhibit pronounced non-linear absorption via a dual mode mechanism involving instantaneous 2PA followed by additional photon absorption due to the excited state absorption (ESA) of the long-lived triplet state.

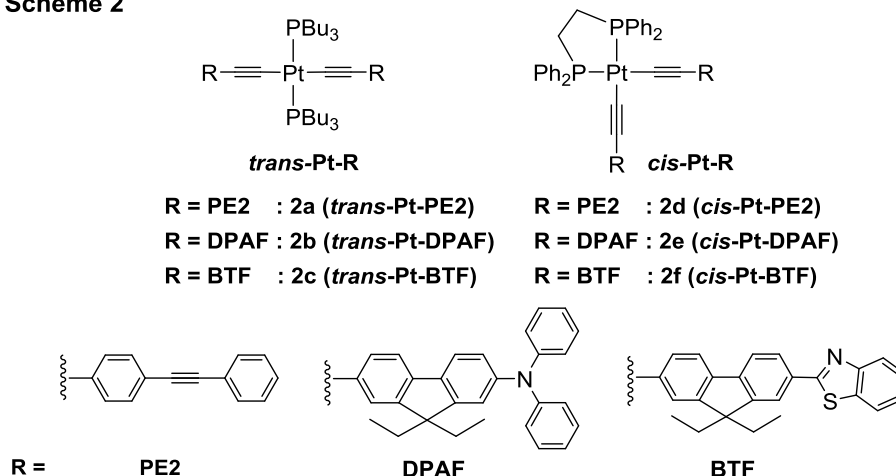
Our work has centered on developing new, high efficiency 2PA/ESA dual mode chromophores, studying their one-photon photophysics and 2PA absorption spectroscopy, and then incorporating selected high efficiency chromophores into matrices in order to afford high efficiency NLA materials. The project has been carried out primarily at the University of Florida, in close coordination with the Agile Limiting group at the Air Force Research Laboratory/Materials and Manufacturing Directorate (AFRL/MLPJ) to complement their ongoing efforts which are related to development of materials for non-linear optical application. Materials developed in the proposed program that exhibit promising non-linear absorption properties have been transitioned to the AFRL/MLPJ group for more extensive testing in specific optical limiting formats. We have also been engaged in collaboration with Prof. Aleksander Rebane of Montana State University, where the 2PA absorption properties of the chromophores and materials are characterized by using femtosecond 2-photon excited fluorescence (2PEF) and non-linear transmittance (NLT) methods. Results are reported in a series of publications,<sup>1-8</sup> and in the following section we highlight specific accomplishments that are relevant to the new proposal.

**III.A. High-Efficiency TPA/ESA Chromophores and Benchmarking.** One objective of the work in this project has been to develop new high efficiency organometallic chromophores that exhibit NLA due to combined 2PA/ESA mechanisms. In order to better understand these chromophores, we have also benchmarked their properties, including measurement of the fundamental photophysical parameters (emission quantum yields, intersystem crossing yields, triplet absorption spectra and absorptivity), as well as their 2PA absorption spectra and cross sections, and their relative NLA response to nanosecond pulses at specific wavelengths.

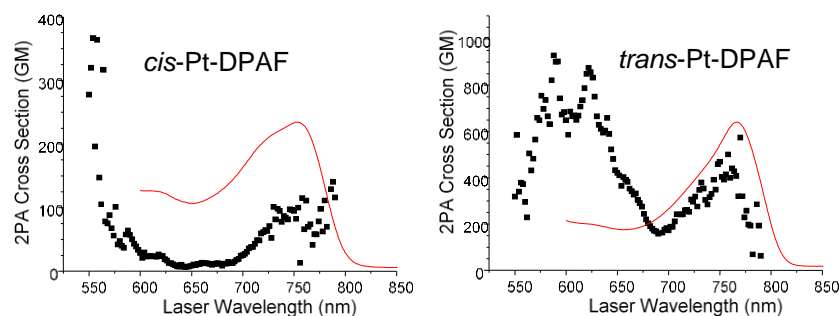
Two chromophores that have been particularly well-characterized and have been benchmarked are *trans*-Pt-DPAF and *trans*-Pt-BTF (**2b** and **2c**, Scheme 2).<sup>3,6,9</sup> These chromophores exhibit moderately efficient 2PA in the 600 – 800 nm region, with peak  $\sigma_2 \sim 200 - 400$  GM. They also display relatively broad triplet-triplet (TT) absorption in the same spectral region as the 2PA, with peak  $\epsilon_{TT} \sim 50 - 80 \times 10^3 \text{ M}^{-1}\text{cm}^{-1}$ . The performance of these chromophores with respect to  $\sigma_2$  and NLT response to nanosecond pulses is approximately one-order of magnitude larger compared to the first-generation **Pt-PE2** chromophore **1a**.<sup>3,6</sup> Chromophores **2b** and **2c** are relatively easy to synthesize and thus have been used extensively as benchmarks to

calibrate other new chromophores and also for use in investigations seeking to fabricate high efficiency NLA materials.

**Scheme 2**



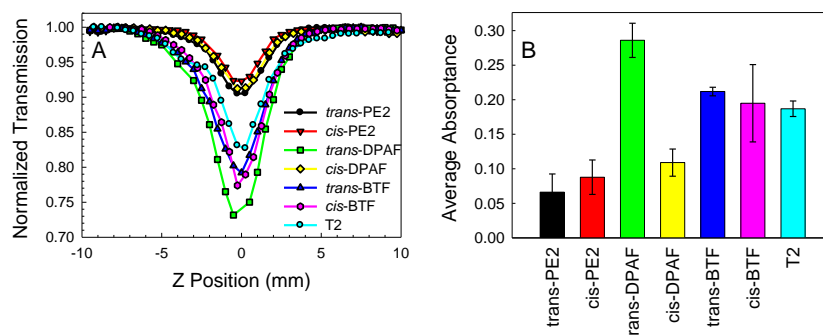
In a line of investigation that is related to the proposed new research, we explored the effects of stereochemistry on the photophysics, 2PA absorption and nanosecond NLA response of the series of chromophores shown in Scheme 2. The photophysical properties of the series are evaluated



**Figure 2.** 2PA spectra of *cis*-Pt-DPAF (**2e**) and *trans*-Pt-DPAF (**2b**) measured by femtosecond fluorescence upconversion (2PEF). Measured by A. Rebane at MSU. Solid line shows ground state absorption ( $2\lambda$ ).

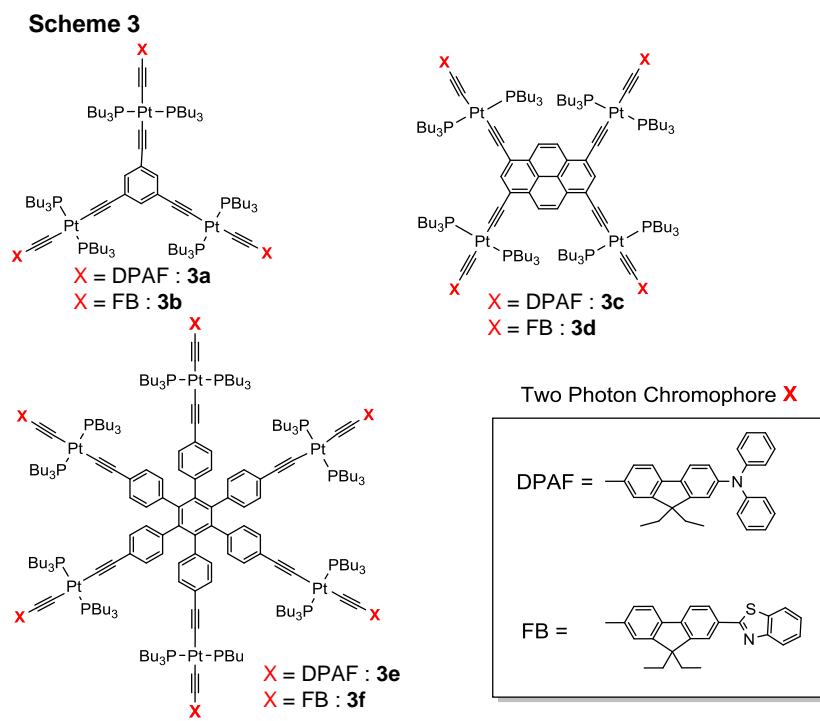
by ground state absorption, steady state emission spectroscopy, and triplet-triplet transient absorption. The NLA was investigated by the nanosecond open-aperture Z-scan and fs fluorescence upconversion techniques by A. Rebane at Montana State University. This work has been fully documented in a paper that is submitted;<sup>6</sup> here we summarize the important aspects of the non-linear response. The 2PA absorption spectra of *trans*-Pt-DPAF (**2b**) and *cis*-Pt-DPAF (**2e**) are shown in Figure 2. The *cis* and *trans* isomeric chromophores display moderate 2PA in the 600 – 800 nm region ( $\sigma_2 > 100$  GM); however, their 2PA spectral response differs. In particular, *cis*-Pt-DPAF displays a 2PA band at  $2\lambda$  for the ground state absorption. This behavior is typical for dipolar, non-centrosymmetric chromophores,<sup>10</sup> and is consistent with the *cis*- geometry. By contrast, *trans*-Pt-DPAF exhibits two 2PA bands, one at  $2\lambda$  for the ground state absorption, and a second band at shorter wavelength. The latter 2PA band is expected for *trans*-Pt-DPAF given its nominally centrosymmetric structure. However, the strong band seen at  $2\lambda$  strongly suggests that there is a mechanism that gives rise to symmetry breaking in this chromophore.<sup>11,12</sup> In separate studies, we have compared the NLA response of these chromophores by nanosecond z-scan, and the results are shown in Figure 3. Interestingly, we find that the response at 600 nm for *trans*-Pt-DPAF is considerably stronger than for *cis*-Pt-DPAF. Given that the TT absorption of the two

systems at 600 nm is very similar,<sup>6</sup> we attribute the stronger response for the *trans* isomer as arising due to its larger  $\sigma_2$  at 600 nm. This result reveals how subtle aspects such as stereochemistry (and symmetry) can influence the 2PA and the NLA response to longer pulses.

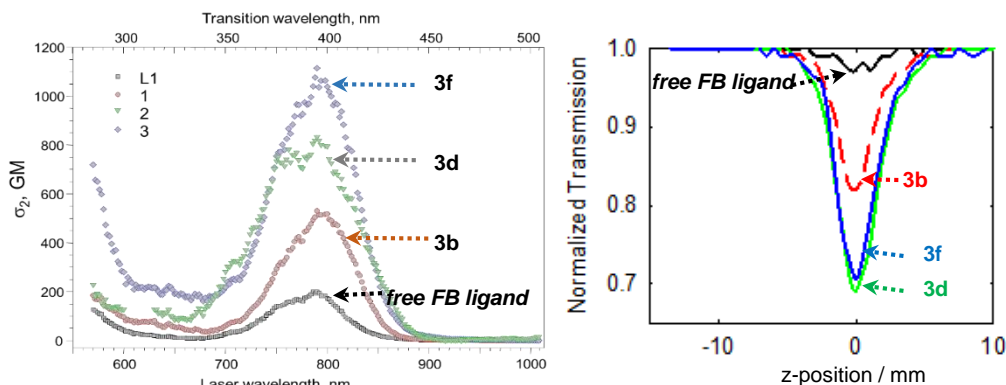


**Figure 3.** A) Open-aperture z-scan response of 1 mM chromophores in THF, ns pulses at 600 nm and 750  $\mu$ J input energy; chromophore structures in Scheme 2. B) Average nonlinear absorptance (1-transmittance) from peak of z-scan. Benchmark chromophore T2 is reported in the literature (ref. 43).

**III.B. High-Efficiency TPA/ESA Polychromophores.** In previous work we and others have demonstrated enhanced  $\sigma_2$  in conjugated systems that feature branched or dendritic architectures.<sup>13</sup> In order to systematically explore the possible synergistic effect of multiple conjugated organometallic chromophores on the 2PA and ESA properties, we investigated the properties of the series of polychromophores shown in Scheme 3. These structures feature multiple 2PA chromophore *arms* and planar,  $\pi$ -conjugated cores. Two well-established 2PA chromophores were incorporated as arms in the poly-chromophores (DPAF and FB structures in Scheme 3).<sup>10,14,15</sup>

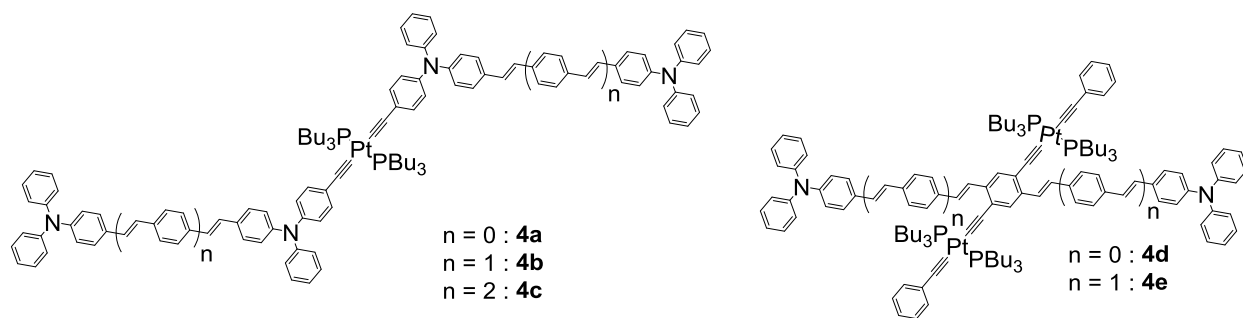


In collaboration with Professor Aleksander Rebane in Montana State University, the 2PA spectra and  $\sigma_2$  for the series of FB poly-chromophores in Scheme 3 were measured and the results are shown in Figure 4a. These 2PA spectra feature absorption between 650 – 875 nm with peaks at about 790 nm, which is nearly degenerate with the 1PA band maxima ( $2\lambda$ ). Note the expected trend, where  $\sigma_2$  increases with the number of 2PA chromophores in the array: **3b** < **3d** < **3f**. A similar trend of increasing NLA response is observed for the nanosecond z-scan in Figure 4b.



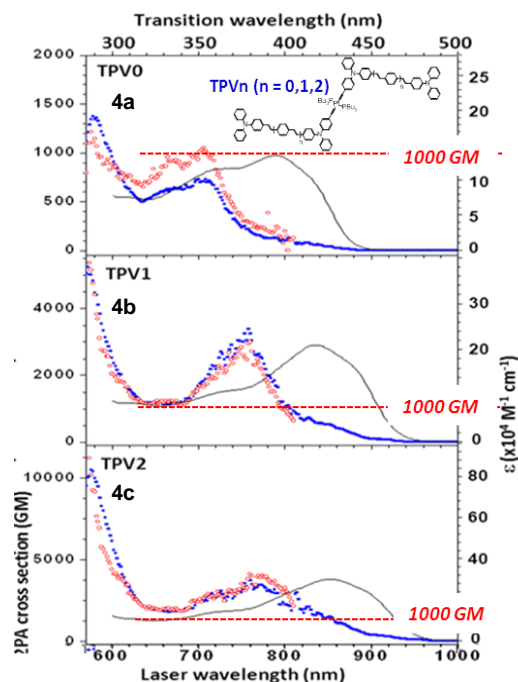
**Figure 4.** a) 2PA spectra for polychromophores **3b**, **3d** and **3f** (Scheme 3) obtained by 2PEF method with 100 fs pulses. b) Open aperture z-scan measurement for **3b**, **3d** and **3f** using nanosecond pulses at 618 nm.

In more recent work, we have designed a new family of platinum containing chromophores that exhibit the largest 2PA cross sections measured for this class of compounds to date.<sup>4</sup> These chromophores incorporate oligo(phenylene vinylene) (OPV) segments capped on each end with **Scheme 4**



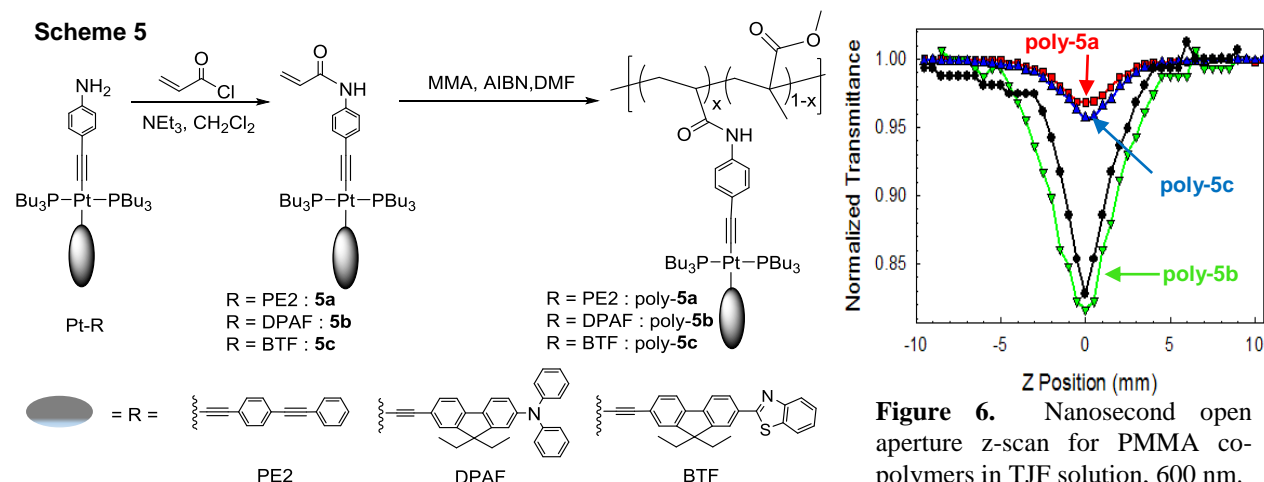
triarylamine donors, and they are linked to the platinum centers via acetylide linkages (e.g., **4a-c**, Scheme 4). In collaboration with Prof. Rebane at MSU, the 2PA spectra of these chromophores have been determined by using a newly developed non-linear transmittance (NLT) technique and some example results are shown in Figure 5. As can be seen, these chromophores exhibit  $\sigma_2 > 1000$  GM over a relatively large spectral range in the near-infrared region; in the case of complex **4c**, the peak value is in excess of 5000 GM. These chromophores also exhibit large triplet-triplet ESA in the near-infrared, and not surprisingly due to the overlap of the 2PA and ESA, they give very large response to nanosecond pulses as measured by open aperture nanosecond z-scan.

One disadvantage of the chromophore design for the **Pt-TPVn** series is that the singlet-triplet intersystem crossing efficiency decreases as the length of the OPV segment increases. Since the triplet yield is important in determining the overall nanosecond NLA efficiency, this trend is undesirable. In a second line of work, we have developed an alternative “cross conjugated” approach to incorporate the OPV segments into platinum acetylide chromophores (**4d,e**, Scheme 4). The cross conjugated chromophores exhibit high 2PA over a broad wavelength region while maintaining > 90% intersystem crossing efficiency. Not surprisingly, the cross conjugated chromophores exhibit among the largest nanosecond NLA response we have measured to date for the platinum acetylide chromophores.<sup>8</sup>



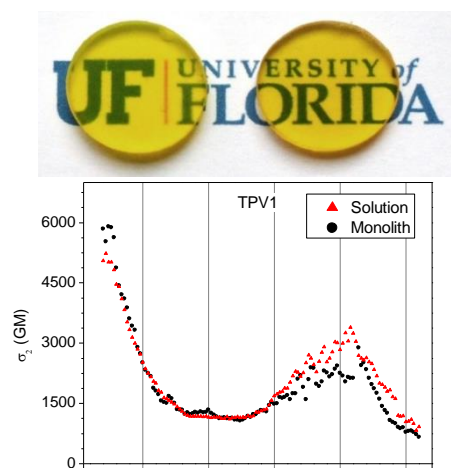
**Figure 5.** 2PA spectra for **Pt-TPVn** (structures **4a**, **4b** and **4c**) with 100 fs pulses. Blue filled symbols: NLT method; red unfilled symbols: 2PEF method; solid line is ground state absorption (wavelength axis at top).

**III.C. Polymer Based Materials for NLA Application** A key aspect of our work has been to develop methods to incorporate the high efficiency 2PA/ESA chromophores into polymeric matrices which will make them amenable for application as optical coatings or elements. In one line of work, Dr. Abigail Shelton developed platinum acetylide complexes that are functionalized with acrylate units allowing them to be incorporated into a poly(methyl methacrylate) glassy host



matrix.<sup>7</sup> Three different monomers were constructed in this work, containing the PE2, DPAF and BTF 2PA chromophores (**5a-c**, Scheme 5). The monomers were co-polymerized with methyl methacrylate to fabricate functional co-polymers that could be studied in solution and cast as solid films or monoliths. The one- and two-photon photophysical properties of the chromophores were preserved in the polymers and good NLA properties were observed when polymer monolith samples were probed with nanosecond pulses in the 600 – 700 nm region. The platinum acetylide monomers could be incorporated into the co-polymers at loadings up to ~10-wt%, corresponding to ~100 mM chromophore concentration in the solid polymers. Increase in loading beyond 10% was not possible because the polymerization was inhibited, apparently by the platinum acetylide unit. This approach to incorporation of high efficiency chromophores into polymers clearly has merit, but the primary disadvantage is the fact that the monomers require multiple synthesis steps for construction, and this limits the amount of polymer available for physical study or application.

In more recent work, we have sought methods to allow direct incorporation of the high efficiency 2PA/ESA chromophores into solid polymer matrices. Here we have developed a technique whereby we make a solution of the chromophore ( $c = 1$  mM) in neat liquid methyl methacrylate (MMA) along with a small amount of a free radical initiator. The resulting MMA solution is heated in a mold for several days under an inert atmosphere. This process allows the fabrication of monolith samples such as those shown in Figure 7. We have fully characterized the photophysics of these glass samples under one- and two-photon excitation. These experiments find that the properties of the chromophores are preserved, including their 2PA absorption (Figure 7b) as well as their nanosecond NLA response. This approach is very promising for application, however, there is one caveat: we have not found it possible to increase the concentration of the chromophores much above 2 mM in the PMMA. Increasing chromophore concentration above this level results in phase segregation, giving rise to scattering in the glass samples.



**Figure 7.** Top: Photographs of PMMA monoliths loaded with 1 mM **4c** and **4d**. Bottom; 2PA spectrum of **4b** in THF solution ( $\blacktriangle$ ) and PMMA monolith ( $\bullet$ ).



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